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CONDITIONING OF FLY ASH WITH SULFAMIC ACID, AMMONIUM SULFATE, AND AMMONIUM BISULFATE

SOUTHERN RESEARCH INSTITUTE

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ABSTRACT

The report summarizes recent experience with three agents—sulfamic acid, ammonium sulfate, and ammonium bisulfate—used to regulate the electrical resistivity of fly ash in electric generating stations to ensure satisfactory collection of fly ash in electrostatic precipitators (ESPs). It presents information about the effectiveness of these agents in pilot- and full-scale ESPs. It also presents the limited information available from practical trials of these agents concerning their conditioning mechanisms. It discusses in detail the fundamental physical and chemical properties of the agents that are relevant to fly-ash conditioning. From this information and the results of ESP tests, the report offers tentative conclusions about conditioning mechanisms. Finally, the report briefly discusses the economic aspects of using each of the agents as a conditioning substitute for sulfur trioxide.

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- Buell Division of Envirotech Corporation
- Environmental Elements Corporation (a subsidiary of Koppers Company)

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SECTION I

CONCLUSIONS

On the basis of the results of precipitator tests discussed in this report, the three conditioning agents reviewed—sulfamic acid, ammonium sulfate, and ammonium bisulfate—appear to be acceptable substitutes for sulfur trioxide if considered only on the basis of their effectiveness in conditioning high-resistivity fly ash. The three agents offer advantages over sulfur trioxide in the ease and freedom from hazard in handling. Ammonium bisulfate, however, does not appear to be worthy of serious consideration as a conditioning agent in the United States because it is apparently not an inexpensive standard commodity. Sulfamic acid seems to be competitive in cost with sulfur trioxide only under limited conditions. Ammonium sulfate appears to be the one of the three agents that is most nearly competitive economically with sulfur trioxide.

Confidential information from industrial sources other than those named in this report makes it desirable to exercise caution in the selection of sulfamic acid or ammonium sulfate over sulfur trioxide as a conditioning agent. Precipitator tests with these agents have not been uniformly successful. As a matter of record, tests with sulfur trioxide have not been uniformly successful either. However, the comparatively limited industrial experience with the newer agents is a factor that should lead to a greater degree of caution in the selection of one of these compounds.

The mechanisms of fly-ash conditioning by sulfamic acid, ammonium sulfate, and ammonium bisulfate include the desired effectiveness in lowering the electrical resistivity of fly ash from low-sulfur coal. However, the physical and chemical processes by which the lowering of resistivity occurs cannot be conclusively identified. The process of conditioning undoubtedly varies as the type of agent, the injection temperature, and the precipitator temperature vary. Even so, the chemical conversion of sulfamic acid or ammonium sulfate to liquid ammonium bisulfate and the coating of fly-ash particles with this conductive substance appear to be important processes in certain instances. The same processes may increase the cohesiveness of fly ash from moderate- to high-sulfur coal and thus aid in coping with the excessive reentrainment of the low-resistivity ash from these fuels.

SECTION II

RECOMMENDATIONS

The research described in this report was limited to a survey of existing knowledge on fly-ash conditioning with sulfamic acid, ammonium sulfate, and ammonium bisulfate. It did not include any experimental work toward evaluating the effectiveness of these conditioning agents or elucidating the mechanisms by which conditioning occurs. From an academic point of view, experimental work in these areas would be desirable. However, from a more practical point of view, the value of further work in these areas must be weighed against the needs for continuing research on other aspects of conditioning including the better known conditioning agents, sulfur trioxide and ammonia.

With consideration having been given to present needs for additional research on the use of conditioning agents, the following recommendations are offered:

- Continuing efforts should be made by the Environmental Protection Agency through its contractors to compile and evaluate new information from the electric power industry on novel conditioning agents including sulfamic acid, ammonium sulfate, and ammonium bisulfate. These efforts should follow the approach described in this report, including an assessment of the practical value of the conditioning agents in specific power plants and an assessment of their value on an industry-wide basis. Specifically, an effort should be made to determine the mechanisms by which conditioning occurs and the range of power-plant conditions where the operation of these conditioning mechanisms will be helpful.

- Experimental work should be undertaken at some future time to resolve questions unanswered by utility trials of novel conditioning agents, in the event that the practical importance of these agents reaches a higher level than that attained thus far.

- Experimental work should be undertaken in the immediate future to resolve unanswered questions about the role in fly-ash conditioning by the

more conventional compounds, sulfur trioxide and ammonia. A broad discussion of new work in this area will be incorporated in a summary report on sulfur trioxide and ammonia conditioning now being prepared for the Environmental Protection Agency by Southern Research Institute. However, an insight to some of the new work needed is given by these questions: (1) Is ammonia an acceptable substitute for sulfur trioxide in treating high-resistivity fly ash from low-sulfur Western coals? (If so, it offers the distinct advantages of lower cost and less difficulty in handling.) (2) Does sulfur trioxide conditioning cause objectionable stack emissions of excess conditioning agent as noxious sulfuric acid mist or sulfate-containing fine particles of fly ash? If so, what are the circumstances under which stack emissions are large enough to be of serious consequence? (The claim is sometimes made that no stack emission of sulfur trioxide vapor occurs, because the fly ash being treated removes all of the material from the flue gas. This claim, however, is disputed by unpublished data recently obtained by Southern Research Institute.) (3) How can sulfur trioxide conditioning be made more generally successful? How can the injection system be designed to avoid the loss of vapor by condensation to an acid mist, which is ineffective for ash conditioning? (There is evidence that deficient designs of injection systems account for some unsuccessful trials of sulfur trioxide conditioning.)

SECTION III

INTRODUCTION

The prevention of excessive emissions of fly ash from coal-burning electric power stations is one of the major current problems in controlling air pollution. This task may be accomplished by the use of high efficiency electrostatic precipitators, liquid scrubbers, and fabric filters. For many years, however, the control of fly-ash emissions has depended mainly on the use of electrostatic precipitators. Currently, the importance of electrostatic precipitators for gas cleaning is continuing; at the same time, the effectiveness of precipitators is being severely challenged by increasingly stringent requirements for the control of fine particles, which are relatively difficult to collect by electrostatic precipitation.

EFFECT OF THE ELECTRICAL RESISTIVITY OF FLY ASH ON THE PERFORMANCE OF AN ELECTROSTATIC PRECIPITATOR

The electrical resistivity of fly ash is one of the most important parameters that control the efficiency of fly-ash removal in coal-burning power stations by the use of electrostatic precipitators. If the resistivity is too high, as it is normally when a low-sulfur coal is burned, the collection efficiency is poor because the electric field between the corona wires and the collecting electrodes falls to a low value, excessive sparking occurs in the interelectrode space, or back corona occurs in the deposited fly ash. Alternatively, if the resistivity is too low, as it may be when a high-sulfur coal is burned, collection efficiency can again be poor because the electrical force holding deposited ash on the collecting electrodes is not high enough to prevent excessive reentrainment during rapping of the electrodes. The upper limit of the acceptable resistivity range is approximately 1×10^{10} ohm cm.[1,2] The lower limit has been defined as values ranging from 1×10^{7} to 1×10^{9} ohm cm.[2,3]

The problem of excessively high electrical resistivity is a more widely occurring problem than that of excessively low resistivity. The problem of high resistivity is becoming increasingly important as the electric utility industry is turning to the use of low-sulfur coal to meet limitations on the emission of sulfur dioxide. The burning of low-sulfur coal lowers the production of sulfur dioxide as desired, but

it also lowers the production of sulfur trioxide or its chemical equivalent, sulfuric acid, with unfavorable consequences on the performance of an electrostatic precipitator in the normal range of operating temperatures, around 150°C.

The conduction of electricity through fly ash at normal precipitator temperatures, around 150°C, occurs primarily through adsorbed gases such as water vapor and sulfur trioxide (or sulfuric acid) that are present on the surfaces of individual fly-ash particles. If the availability of sulfur trioxide is lowered as the result of the combustion of low-sulfur coal, the electrical resistivity of the fly ash will be raised.

Maintaining a sufficiently low electrical resistivity is important without regard to the size of fly-ash particles being collected. However, it is extremely important in limiting the emission of small particles, having diameters less than 2 μm. To charge small particles effectively, high current densities in a precipitator are essential, and they can only be maintained effectively if the resistivity of the fly ash is not excessive.

CONTROL OF ELECTRICAL RESISTIVITY PROBLEMS BY CHEMICAL CONDITIONING

The technology referred to as "conditioning" provides a means of coping with the high electrical resistivities found with fly ash from low-sulfur coal. Usually, a conditioning agent is used specifically for this purpose. In some instances, however, a conditioning agent may be used to cope with unusually low resistivities. In still other instances, moreover, the phenomenon produced by a conditioning agent may not involve the resistivity to any degree. As pointed out subsequently, a conditioning agent may affect the cohesiveness of fly-ash particles rather than the resistivity of the particles, and it may also produce a space-charge effect in which there is a change in the electrical properties of the flue gas rather than the fly ash. In this report, the term conditioning is used to embrace the use of all chemical additives for improving the collectibility of fly ash in an electrostatic precipitator, regardless of the mechanism of action of the additives.

The best known method of conditioning fly ash is to inject either sulfur trioxide or sulfuric acid vapor into the flue-gas stream ahead of a precipitator.[1-9] Injection of sulfur trioxide or sulfuric acid vapor supplements the quantity of this substance that is produced naturally, and the most likely explanation of this conditioning method is that the flue-gas additive lowers the resistivity of the fly ash.

Ammonia is a conditioning agent that is sometimes used in place of sulfur trioxide or sulfuric acid.[10-12] Injection of this compound may, under certain circumstances, lower the resistivity of fly ash from low-sulfur coal. It appears doubtful that this mechanism of conditioning by ammonia has ever been conclusively demonstrated; certainly, all efforts by Southern Research Institute to demonstrate this effect have been unsuccessful.[13] Even so, there is adequate evidence that ammonia sometimes improves the collectibility of high-resistivity ash by some mechanism. Injection of ammonia into the flue gas from a high-sulfur coal may help in overcoming the problems associated with low-resistivity fly ash. Mechanisms of conditioning under these circumstances apparently do not involve any significant change in resistivity, but they do seem to involve an enhancement of the electric field in a precipitator through a space-charge effect and an enhancement of the forces of cohesion binding together individual fly-ash particles, thus lowering reentrainment losses.[13]

Flue-gas additives in addition to sulfur trioxide and ammonia that improve the electrostatic precipitation of various types of particulate substances include organic amines, inorganic acids, and inorganic salts.[14,15] Specific examples of compounds in these categories are (1) ethyl, diethyl, and triethyl amines; (2) phosphoric and sulfamic acids; and (3) ammonium sulfate, ammonium bisulfate, calcium chloride, sodium chloride, and sodium sulfate. At present, there is an appreciable interest in the utility industry in three of these compounds: sulfamic acid, ammonium sulfate, and ammonium bisulfate. The following sections of this report give the results of a survey to determine the utility of these three compounds as flue-gas additives in competition with sulfur trioxide or sulfuric acid.

Conditioning of fly ash may be accomplished not only by the use of flue-gas additives but by the use of boiler additives. Recent publications have indicated that the addition of compounds of sodium and iron to the coal fed to a boiler provides a practical basis for lowering the resistivity of the fly ash produced.[16,17] The greatest value of these boiler additives may occur in power stations using so-called "hot" precipitators, which collect fly ash from flue gas around 300 to 350°C. At these temperatures, the conduction of electricity through fly ash takes place by ion migration through the interior rather than along the surface of individual particles. There is the possibility, however, that boiler additives may be beneficial at lower precipitator temperatures where surface rather than volume conduction is predominant.

SECTION IV

TECHNICAL BACKGROUND

Much of the current interest in sulfamic acid, ammonium sulfate, and ammonium bisulfate as conditioning agents for fly ash apparently originated with the thought that these compounds would be conveniently handled sources of sulfur trioxide. Theoretically, these compounds can be thermally decomposed to sulfur trioxide in hot flue gas, as indicated by the following chemical equations:

$$H_2NSO_3H \rightarrow NH_3 + SO_3 \quad (1)$$

$$(NH_4)_2SO_4 \rightarrow 2NH_3 + H_2O + SO_3 \quad (2)$$

$$NH_4HSO_4 \rightarrow NH_3 + H_2O + SO_3 \quad (3)$$

The handling of sulfur trioxide and its chemical equivalent, sulfuric acid, is difficult in a power plant because both compounds are highly corrosive and toxic liquids that must be vaporized before injection into flue gas. The handling of sulfamic acid, ammonium sulfate, or ammonium bisulfate, on the other hand, is not a source of significant difficulty. Both of these compounds exist as relatively noncorrosive and nontoxic solids at ambient temperatures; they can be injected into a flue-gas stream as a powdered solid or, alternatively, they can be dissolved in water and injected as an aqueous spray.

One trend of thought about the use of sulfamic acid, ammonium sulfate, and ammonium bisulfate has been described by Lowe of the Central Electricity Research Laboratories in Great Britain.[18] Lowe's publication indicates that interest was initially focused on sulfamic acid in the belief that this compound would serve as a convenient source of sulfur trioxide, as shown in Equation 1. However, Lowe reports the discovery that sulfur trioxide is only a minor product of the decomposition of sulfamic acid and that ammonium bisulfate is a far more significant product. The decomposition process yielding ammonium bisulfate is much more complex than that yielding sulfur trioxide as shown by Equation 1. In any event, Lowe indicates that promising results obtained with sulfamic acid

led to direct trials of ammonium bisulfate as an alternative conditioning agent and later to trials of ammonium sulfate. This compound may be thermally decomposed to the bisulfate as shown by this chemical equation:

$$(NH_4)_2SO_4 \rightarrow NH_3 + NH_4HSO_4 \qquad (4)$$

The decomposition of ammonium sulfate shown by Equation 4 is obviously less extensive than that previously shown by Equation 2 and would be expected to occur at lower temperatures.

A rather different trend of thought led the Koppers Company to investigate ammonium sulfate and ammonium bisulfate as conditioning agents for fly ash.[19] Prior to its consideration of these two compounds, the Koppers Company had extensive experience with ammonia as a conditioning agent.[10] This experience showed that ammonia was effective in conditioning fly ash from moderate- to high-sulfur coal but rarely effective in conditioning fly ash from low-sulfur coal. The conclusion was that ammonia was effective only when naturally produced sulfur trioxide was present at a sufficient concentration to react with ammonia in the presence of water vapor to produce either ammonium sulfate or ammonium bisulfate. Either of these compounds could be formed by the reversal of Equation 2 or 3 at sufficiently low flue-gas temperatures.

Interest in sulfamic acid, ammonium sulfate, and ammonium bisulfate as conditioning agents has undoubtedly been stimulated by a recent publication by Dalmon and Tidy of the Central Electricity Research Laboratories in Great Britain.[15] This paper compares these and other novel conditioning agents with sulfur trioxide and ammonia. Dalmon and Tidy used a laboratory-scale precipitator for investigating various types of conditioning agents, which are classified below as to physical state at ambient temperatures:

- Gaseous compounds—sulfur trioxide, hydrogen chloride, and ammonia
- Liquid sulfuric acid (injected at a concentration of 0.11 to 9.4 M in water)
- Solid compounds derived from sulfur trioxide and ammonia—sulfamic acid, ammonium sulfate, and ammonium bisulfate (injected as solids or solutes in aqueous solutions at concentrations of 0.23 to 1.8 M)

- Solid inorganic salts—sodium chloride, sodium sulfate, calcium chloride, and lithium iodide (injected as solutes in aqueous solutions at concentrations of 0.45 to 1.8 M)

The particulate conditioned with these agents was water-washed fly ash from a coal-fired power station. The gas stream containing the fly ash was produced by combustion of a low-sulfur paraffin and adjusted in composition by the addition of water vapor to a humidity level of about 8% by volume. The gas stream was essentially free of sulfur dioxide except when this gas was added deliberately to obtain a better approximation of the composition of flue gas from a low-sulfur coal.

Dalmon and Tidy reported that each additive to the gas stream improved the efficiency of fly ash collection in the absence of added sulfur dioxide, with the degree of improvement usually being controlled by the efficiency of uptake of the conditioning agent by the fly ash. They reported, however, that only a limited number of these additives improved the collection efficiency in the presence of added sulfur dioxide, which itself caused a significant improvement if added at concentrations of 100 to 300 ppm by volume, as found in flue gas from low-sulfur coal. The only additives effective in the presence of sulfur dioxide—that is, under the conditions better simulating a flue-gas environment—were sulfur trioxide, sulfuric acid, sulfamic acid, ammonium sulfate, ammonium bisulfate, and ammonia. Among these compounds, ammonia was effective only if hydrogen chloride (one of the normal constituents of flue gas) was also added to the gas stream investigated under laboratory conditions. (It is possible that ammonia might have been effective if sulfur trioxide had been added in place of hydrogen chloride but ammonia was not evaluated with sulfur trioxide as a secondary additive.)

Successful trials of sulfamic acid and ammonium sulfate have been made in full-scale power plants in both Great Britain and the United States. The trials in Great Britain have been made under the auspices of the Central Electricity Generating Board, which was responsible for the previously described work of Dalmon and Tidy[15] and Lowe.[16] The trials in the United States have been made by several utility companies with the aid of two companies supplying the two conditioning agents: (1) Apollo Chemical Corporation, which supplies a proprietary blend of sulfamic acid with other chemicals that is known as "Coaltrol PPA-30" (a powder) or "Coaltrol LPA-40" (an aqueous solution); and (2) Environmental Elements Corporation (subsidiary of the Koppers Company), which supplies ammonium sulfate as the product "Koppers K." There appears to have been no evaluation of ammonium bisulfate in any full-

scale power plant either abroad or in this country, perhaps because of the greater cost of this chemical and the lack of availability of the chemical as a commercial item.

In this report, sulfamic acid is regarded as the essential constituent of the agents supplied by Apollo Chemical Corporation. This compound is clearly the primary constituent in terms of weight percentage, as described in the Appendix of this report. The minor constituents may play some role in the conditioning of fly ash, but they have not been characterized sufficiently to warrant any speculation about their role in conditioning.

Insofar as Koppers K is concerned, there is no reason for believing that the conditioning agent contains any active compound except ammonium sulfate. Presumably, any other compounds present are normal impurities in the commercial grade of ammonium sulfate.

SECTION V

PRECIPITATOR TESTS OF SULFAMIC ACID AS A CONDITIONING AGENT

PILOT-PLANT TESTS

A brief discussion of Damon and Tidy's pilot-scale precipitator tests including sulfamic acid and other conditioning agents[15] has already been given in Section IV. A more complete discussion of those tests involving sulfamic acid is given in the following paragraphs.

In the pilot-plant precipitator tests performed by Dalmon and Tidy, sulfamic acid was injected upstream from the precipitator at a temperature of 400 or 165°C. At the higher temperature, the agent was injected either as a powder or as an aqueous solution (0.45 M); at the lower temperature, the agent was injected only in the aqueous form. The conditioned fly ash was then collected in the precipitator at a temperature of 145°C.

Dalmon and Tidy made determinations and calculations of the following:

- Precipitator efficiency
- Precipitation rate parameter w_p (cm/sec)

$$w_p = -[\ln(1-E)]/k$$

where E = precipitator efficiency

k = 0.315 sec/cm (a constant based on the precipitator geometry and the flow rate of the gas stream)

- Uptake of sulfamic acid by the fly ash
- Sparkover voltage of the precipitator
- Electrical resistivity of the fly ash at the precipitated bulk density and at a constant bulk density of 0.975 g/cm^3

The investigators found that injection of sulfamic acid in solution was much more effective than injection of the agent as a solid. Using the solution method of injection, they found that the uptake of about 0.8% by weight produced the following desirable changes:

- Precipitation rate parameter—increased from 9.5 to 14 cm/sec
- Sparkover voltage—increased from 42 to 49 kV
- Resistivity—lowered from about 1×10^{14} to 1×10^{13} ohm cm at a bulk density of 0.975 g/cm^3

Uptake of sulfamic acid by the fly ash was judged on the basis of the quantity of soluble sulfate ion found in the conditioned ash. The analysis of soluble constituents of the ash indicated that the sulfamic acid was decomposed to a sulfate, perhaps ammonium bisulfate as the initial product. However, little ammonium ion was found with the sulfate ion, and the explanation offered was that strong bases in the fly ash reacted with ammonium ion and allowed ammonia to be lost by volatilization. (Although the fly ash had been water-washed prior to use, it was highly basic, producing a pH of 11 in a 10%-by-weight slurry in water. No further information about the chemical properties of the ash was published.)

FULL-SCALE TESTS

The following paragraphs summarize information about trials of sulfamic acid in one British power station and in three American power stations. In the British station, the conditioning agent was presumably the ordinary commercial form of sulfamic acid. In each of the American stations, on the other hand, the agent was the blend with other chemicals that is supplied by Apollo Chemical Corporation as a powdered solid.

Rugeley Power Station (Great Britain)

Dalmon and Tidy have given a brief summary of precipitator tests with sulfamic acid at the Rugeley Power Station in Great Britain.[15] They state that the conditioning agent was added to the flue gas ahead of the air preheater at a temperature of 500°C by spraying an aqueous solution having a concentration of 1.3 M. The concentration thus injected in the flue gas was 20 ppm by volume, based on the assumption that complete volatilization occurred without decomposition (this assumption is used only as a convenient basis for comparing

the rate of injection with the rates of injection of gaseous conditioning agents such as sulfur trioxide and ammonia). The emission of fly ash was reportedly lowered by 55%.

Cabin Creek Power Station (Appalachian Power Company)

The most extensive investigation of sulfamic acid in the American utility industry apparently has been made at the Cabin Creek Station of Appalachian Power Company, a subsidiary of American Electric Power Company. Cabin Creek Station is located in West Virginia, where state law requires a maximum dust emission rate of 0.09 mg/kcal (0.05 lb/10^6 Btu) but prohibits the use of sulfur trioxide as a conditioning agent to reach this emission rate when low-sulfur coal is burned to minimize sulfur dioxide emission. Thus, Appalachian Power Company undertook an investigation of sulfamic acid to determine whether use of this agent would permit compliance with the state requirements.

The utility company investigated sulfamic acid as a flue-gas additive when coals normally available were burned. The company also investigated this additive when certain "metallurgical" coals (low in ash content) were burned on an experimental basis, even though these coals were not available in sufficient amount for sustained use. Sulfur percentages in the various coals were in the range of 0.8 to 1.0% except in one instance where the value was 1.4%. Some of the results of the precipitator tests at Cabin Creek Station were published in a technical bulletin by the supplier of the sulfamic acid.[20] More extensive data from these tests were provided for publication in this report by a representative of the American Electric Power Service Corporation.[21]

At Cabin Creek Station, sulfamic acid was injected as a powder into the flue gas produced in each of two boilers with rated loads of 50 MW (each boiler was one of a pair comprising one unit with a rated load of 100 MW). The site of injection was the duct upstream from the economizer, where the flue-gas temperature was approximately 625°C. The treated gas stream then passed through a precipitator where the temperature averaged about 185°C in one instance or about 160°C in another instance. Coals from three different sources with ash contents of about 10% by weight were burned in one boiler, whereas coals from four other sources with ash contents of only 6% were burned in the second boiler.

Table 1 summarizes the conditions under which sulfamic acid was investigated and gives comparative precipitator efficiencies with and without this additive. This table lists rates of sulfamic acid injection as a weight fraction of the rate of coal consumption. Calculations indicate that 1 part of

Table 1. RESULTS OF PRECIPITATOR TESTS AT CABIN CREEK STATION WITH SULFAMIC ACID AS A FLUE-GAS ADDITIVE[a]

Coal			Boiler load, MW	Additive rate,[b] parts per 2000 parts of coal	Precipitator efficiency,[c] %
Type	% S	% Ash			
CI	1.4	9.7	48	1.1	98.6
			36	1.4	98.7
			33	2.0	99.1
C	0.9	10.4	32	0	91.0
			39	1.3	98.2
E	0.9	10.3	40	0	98.1
			44	1.1	97.2
			36	1.3	98.8
			42	1.6	99.0
ON	1.0	6.0	45[d]	0	95.3
			42	1.3	95.1
IC	1.0	5.7	51[d]	0	68.9
			50	0.5	88.2
			52	1.1	87.6
			52	2.0	94.0
AS	0.8	5.7	45[d]	0	95.3
			45	1.2	95.1
A	0.8	5.1	47[d]	0	78.6
			44	1.0	89.7
			45	1.8	84.6

[a] Most of the data presented are averages computed from the results of several tests.
[b] To calculate the approximate concentration in the gas stream in parts per million by volume, multiply the values listed by the factor 10.
[c] Average gas temperatures were 185°C with Coals CI, C, and E and 160°C with Coals ON, IC, AS, and A.
[d] Not reported but estimated from comparative values of the rate of steam production.

sulfamic acid to 2000 parts of coal corresponds to roughly 10 ppm by volume of the conditioning agent in the flue gas (based on the assumption of complete volatilization of the agent without thermal decomposition). The efficiency data indicate that conditioning with sulfamic acid produced favorable results with all of the coals except two (Coals ON and AS). However, an analysis performed by the Appalachian Power Company led to the conclusion that the only statistically significant improvement occurred with Coal IC.

For each of the coals investigated, a precipitator efficiency of 99% or greater is needed to satisfy the maximum dust emission level of 0.09 mg/kcal. From Table 1, it appears that the maximum additive rates used permitted this requirement to be approximated with Coals CI and E but not with the other fuels. The statistical study cited above led to the conclusion that the improvement in precipitator performance attained with sulfamic acid was not enough to meet the emission standard with coals of high emission levels and that the improvement was inconsequential with coals of low emission levels.

Table 2 summarizes the results of fly ash analyses that were performed at the Cabin Creek Station. One of the most striking aspects of the analytical information is the loss-on-ignition data. These data indicate that the combustion efficiency in the boilers was always low but especially low when the low-ash fuels (Coals ON, IC, AS, and A) were burned. The oxide percentages show this primary difference: the low-ash coals had lower soda and lime contents but higher sulfur trioxide contents. Determinations of total sulfur trioxide, water-soluble sulfur trioxide, and pH were not always performed. However, the apparent effect of the conditioning agent on these ash properties was that the agent lowered the pH of ash from four of five coals and increased the soluble sulfur trioxide on the ash from three of four coals for which the data are available. These effects suggest that sulfur trioxide from decomposed sulfamic acid was deposited on the ash, although occurrence of this effect is not consistently confirmed by the available data.

Table 3 shows the results of determinations of the concentrations of sulfur dioxide, sulfur trioxide, and ammonia at the outlet of the precipitator during the tests with Coals CI, C, and E. The concentrations of sulfur dioxide are about as expected from coals containing 0.9 to 1.4% sulfur considering the large excess of air that was present in the gas stream. The concentrations of sulfur trioxide were all reported as "nil." The minimum concentration of sulfur trioxide that was detectable by the experimental method was not reported; however, it can be concluded that the injection of the conditioning agent caused no perceptible increase in the concentration

Table 2. RESULTS OF FLY-ASH ANALYSES AT CABIN CREEK STATION WITH AND WITHOUT SULFAMIC ACID AS A FLUE-GAS ADDITIVE

Coal burned	LOI, %[a]	Constituent of fly ash[a]							Total SO_3, %[b]		Soluble SO_3, %[b]		pH[b]	
		Na_2O, %	K_2O, %	CaO, %	MgO, %	Al_2O_3, %	Fe_2O_3, %	SiO_2, %	w/o	w/	w/o	w/	w/o	w/
CI	10.3	0.7	0.3	3.8	-	(total,	38.2)	56.4	-	-	-	-	-	-
C	12.7	0.6	0.3	3.9	0.6	22.0	13.2	58.0	-	-	-	-	8.8	9.0
E	35.5	0.7	0.3	4.9	0.3	26.2	13.9	57.0	-	-	-	-	-	-
ON	39.4	Tr	0.6	Nil	Tr	29.2	18.1	51.4	-	-	0.3	0.6	7.8	5.8
IC	39.7	Nil	0.6	Nil	0.5	36.5	7.8	51.1	1.7	1.4	0.7	0.9	4.3	4.1
AS	49.3	0.2	0.4	Nil	0.2	38.9	4.9	50.5	1.6	1.9	1.2	1.5	5.4	4.6
A	40.5	Nil	0.3	Nil	0.3	35.1	3.7	59.3	1.3	1.0	0.8	0.8	4.7	4.4

[a] LOI indicates loss on injection. Oxides percentages are for the ash after ignition. Tr indicates that only a trace was detected.

[b] The symbol w/ indicates that the additive was present, and the symbol w/o indicates its absence. Soluble SO_3 is the material dissolved in a 1% aqueous slurry. The pH value is for this slurry after 15 min of stirring.

Table 3. RESULTS OF GAS ANALYSES AT CABIN CREEK STATION WITH AND WITHOUT SULFAMIC ACID AS A FLUE-GAS ADDITIVE[a]

Coal	Additive rate, parts per 2000 parts of coal	Gas concentrations, ppm		
		SO_2	SO_3	NH_3
CI	1.1	420	-	2.7
	1.3	414	Nil	2.8
C	0	332	Nil	Nil
	1.3	430	-	Nil
E	0	305	Nil	Nil
	1.1	316	Nil	0.3
	1.6	343	-	1.0

[a]The data presented are averages computed from the results of several determinations.

of effluent sulfur trioxide, despite the expected formation of this compound from the decomposition of sulfamic acid. Perhaps the most noteworthy aspect of the gas determinations is that ammonia was usually found during conditioning, showing that at least partial decomposition of the sulfamic acid did occur.

Mercer Station (Public Service Electric and Gas Company, New Jersey)

Apollo Chemical Corporation has reported favorable results with sulfamic acid at the Mercer Station of the Public Service Electric and Gas Company in New Jersey.[22,23] The data published from this power station are summarized in Table 4. These data support the claim that the injection of 1 part of conditioning agent per 2000 parts of coal brought the emission to a level below the maximum allowed by state law;[22] however, other data published for this station indicate that the preferred additive rate is 2.5 parts of conditioning agent per 2000 parts of coal.[23]

A representative of the utility company has confirmed that the conditioning agent gives a distinct improvement in precipitator performance but has not agreed to release information beyond that summarized in Table 4.[24] This source of information has indicated that the use of sulfamic acid is continuing at the Mercer Station, whereas it has been discontinued at the Cabin Creek Station.

Table 4. RESULTS OF PRECIPITATOR TESTS AT MERCER STATION WITH SULFAMIC ACID AS A FLUE-GAS ADDITIVE[a]

Sulfur percentage in coal	Additive rate, parts per 2000 parts of coal	Emission rate, mg/kcal (lb/10^6 Btu)[b]
0.96	0	0.39 (0.22)
	0.50	0.11 (0.06)
	0.75	0.17 (0.09)
	1.00	0.09 (0.05)
	4.00	0.08 (0.05)
1.47	0	0.32 (0.18)
	1.20	0.13 (0.07)

[a]Mercer Station boiler rating, 300 MW. Additive injected at gas temperature of about 425 to 480°C.
[b]Emission allowed, 0.18 mg/kcal (0.1 lb/10^6 Btu).

Station A (Unidentified Utility Company)

The Buell Division of Envirotech Corporation investigated sulfamic acid as a conditioning agent in two units of a power generating station designated as Station A.[25] These two units have power-generating capacities of about 25 MW and are equipped with electrostatic precipitators having design efficiencies of 95.0% in cleaning flue gas at temperatures of about 190°C. Neither precipitator operates at the design efficiency, however, when collecting fly ash from the coal that is now customarily used as a fuel at Station A.

The coal normally burned at Station A contains about 1% of sulfur and 9% of ash constituents. The fly ash produced from this coal typically has the composition given in Table 5. Laboratory measurements of the electrical resistivity of the ash indicate that the value is typically about 1×10^{12} ohm cm at the gas temperature where the ash is collected in the precipitators.

Sulfamic acid was investigated as a conditioning agent to determine whether it would allow the precipitators to reach or exceed their design efficiencies. In the two units of Station A, the conditioning agent was injected as a powder at locations upstream from the air preheaters where the estimated flue-gas temperatures exceed 600°C. The injection rates ranged from 0.5 to 1.5 parts by weight of the conditioning agent for each 2000 parts by weight of the coal being burned. The performance of the precipitators with the

Table 5. RESULTS OF FLY-ASH ANALYSIS AT STATION A

Constituent[a]	Percentage by weight
Na_2O	0.4
K_2O	2.5
MgO	0.7
CaO	1.4
Al_2O_3	27.0
Fe_2O_3	6.2
SiO_2	48.5
TiO_2	0.7
P_2O_5	0.3
SO_3	0.8

[a]Loss on ignition, 7.6%.

conditioning agent present was based on determinations of efficiency in some of the tests and determinations of precipitator currents and observations of stack emission in other tests.

Efficiency data from four tests of one unit were made available by Buell for citation in this report. With the feed rate of sulfamic acid set as 1 part of the agent to 2000 parts of coal, measured efficiencies were 96.1, 98.5, 98.8, and 99.1%. All of these efficiencies exceeded the design value of 95.0% as desired, and they were well above the values averaging about 90% without conditioning. Characteristically, injection of sulfamic acid increased the precipitator currents and improved the appearance of the stack emission. The change in precipitator currents implies that the electrical resistivity of the fly ash was lowered by the conditioning agent.

Buell appears to be satisfied with the performance of sulfamic acid as a conditioning agent except for one problem that it created: plugging of the air preheaters, which are of the tubular type at Station A. This problem is regarded as severe enough to make sustained use of sulfamic acid impractical at this power station. Another reported disadvantage of sulfamic acid is its relatively high cost as a conditioning agent in comparison with sulfur trioxide or sulfuric acid.

SECTION VI

PRECIPITATOR TESTS OF AMMONIUM SULFATE AND AMMONIUM BISULFATE AS CONDITIONING AGENTS

PILOT-PLANT TESTS

Pilot-plant evaluations of ammonium sulfate and ammonium bisulfate fall into two categories. One investigation was carried out by Dalmon and Tidy in a laboratory-scale precipitator,[15] as discussed previously in this report. Other investigations were conducted by the Koppers Company with a substantially larger pilot-scale precipitator,[19] which was transported to various power stations and used to collect fly ash from the flue gas generated in these stations.

Investigation by Dalmon and Tidy[15]

This study of ammonium sulfate and ammonium bisulfate was very similar to the study of sulfamic acid by the same investigators, as described in Section V. Each compound was injected as a powder at a gas temperature of 400°C or as an aqueous solution at the same temperature or a lower temperature, 165°C. Each compound was much more effective when injected in a solution. Ammonium sulfate was injected at various concentrations ranging from 0.23 to 1.80 M, whereas ammonium bisulfate was injected only at a concentration of 0.45 M.

Each compound increased the precipitation rate parameter and the sparkover voltage and lowered the electrical resistivity of the fly ash to a degree dependent on the uptake of the compound by the ash. The effectiveness of each compound in making any of these changes in the precipitation parameter was comparable to the effectiveness of sulfamic acid if compared on the basis of the uptake in moles of conditioning agent per unit weight of fly ash.

Like sulfamic acid, ammonium sulfate and ammonium bisulfate were found in the fly ash mainly as sulfate ion. The quantity of ammonium ion found was never as high relative to the quantity of sulfate to match the stoichiometry of 2:1 for ammonium sulfate or 1:1 for ammonium bisulfate. Loss of ammonium ion as ammonia gas was assumed to occur as the result of the basic nature of the fly ash.

Investigations by the Koppers Company[19]

Pilot-plant precipitator data have been obtained by the Koppers Company with ammonium sulfate as the conditioning agent in three power stations and with ammonium bisulfate as an alternative agent in one of these plants. These three plants are referred to in this report as Stations B, C, and D.

The test conditions and the results are summarized in Table 6. It will be noted that the electrical resistivities of unconditioned fly ash in the three plants varied widely. The resistivity at Station B was only 1×10^7 ohm cm. The resistivity at Station C was 1×10^{10} ohm cm, which is cited as the upper limit for satisfactory operation of an electrostatic precipitator.[1,2] Finally, the value at Station D was quite high, 1×10^{13} ohm cm. Despite the wide range in resistivities, the performance of the precipitator was improved in each instance by the injection of the conditioning agents at a concentration equivalent to 15 ppm by volume (a hypothetical value assuming volatilization without decomposition).

Table 6. RESULTS OF PRECIPITATOR TESTS BY THE KOPPERS COMPANY WITH AMMONIUM SULFATE OR AMMONIUM BISULFATE AS THE CONDITIONING AGENT

Station	Sulfur in coal, %	Gas temp, °C	Fly-ash resistivity,[a] ohm cm	Conditioning agent[b]	Outlet ash concn,[c] g/m³
B	2.5	150	1×10^7	None	0.27
				$(NH_4)_2SO_4$	0.12
				NH_4HSO_4	0.11
C	1.0	150	1×10^{10}	None	0.30
				$(NH_4)_2SO_4$	0.16
D	0.5	130	1×10^{13}	None	0.058
				$(NH_4)_2SO_4$	0.016

[a] Determined in the laboratory with the temperature and water-vapor concentration duplicating these conditions at the plant.

[b] Injected ahead of the precipitator in an aqueous solution at the gas temperature given in the third column. Intended to produce an effective concentration in the flue gas of 15 ppm by volume, based on the hypothetical volatilization of the compound without decomposition.

[c] To convert to concentration in gr/ft³, divide the concentration listed by 2.3.

The results obtained at Stations B and C are the only data cited in this report where the collection of fly ash of low to moderate resistivity was improved by a conditioning agent. It must be assumed that in these instances the mechanism of conditioning was not a lowering of resistivity but some other effect, perhaps a space-charge effect or an increase in the cohesiveness of the ash. These latter mechanisms of conditioning are discussed in Section VIII of this report.

The results obtained at Station D almost certainly reflect conditioning through the mechanism of lowered resistivity. This conclusion is supported by measurements of electrical parameters of the precipitator. Without conditioning, the secondary voltage and current were 38.0 kV and 10.4 mA. With conditioning, the values of these parameters increased to 41.4 kV and 25.7 mA. (No electrical data for Stations B and C are available for inclusion in this report. Also, no resistivity data for conditioned ash in any of the plants are available for presentation.)

FULL-SCALE TESTS

Dalmon and Tidy have reported trials of ammonium sulfate at two power stations in Great Britain where the electrical resistivity of the fly ash was presumably excessive.[15] At Rugeley Station, the compound was injected as an aqueous spray ahead of the air preheater at a temperature of 500°C to produce an effective concentration in the gas stream of 20 ppm; it lowered the emission of fly ash by 55%, as did sulfamic acid under similar conditions (Section V). At the Aberthaw Station, the compound was injected as an aqueous spray upstream from the air preheater at 300°C or downstream from the preheater at 150°C; the rate of injection at either temperature was controlled to produce an effective concentration in the flue gas of 25 ppm. At Aberthaw, the conditioning agent lowered the emission of fly ash by 65% when injected at the higher temperature or 41% when injected at the lower temperature.

The Koppers Company has reported the results of conditioning with ammonium sulfate at one full-scale power station in the United States.[19] The agent was injected downstream from the air preheater at a temperature of 140°C to produce a concentration of 15 ppm in the flue gas. The fly ash in this plant was produced from a low-sulfur coal and had a high electrical resistivity, 1×10^{12} ohm cm as measured under laboratory conditions. The conditioning agent lowered the emission of fly ash by 50%, presumably as a result of its lowering of the resistivity of the ash.

SECTION VII

FUNDAMENTAL PROPERTIES AND CONDITIONING MECHANISMS OF SULFAMIC ACID

PHYSICAL AND CHEMICAL PROPERTIES

The fundamental physical and chemical properties of sulfamic acid at both ambient and elevated temperatures are important in the use of this compound as a conditioning agent for fly ash. The properties at ambient temperatures are relevant in a practical sense to the methods used for handling the compound and injecting it into flue gas, which involve either the dry solid or an aqueous solution. The properties at elevated temperatures, on the other hand, are important theoretically in explaining the mechanisms by which the compound acts as a conditioning agent.

Ambient Temperatures[26-31]

Pure sulfamic acid exists as a white crystalline solid at ambient temperatures. It is quite stable through a wide range of temperatures, even up to its melting point of 205°C. In contrast to sulfuric acid, to which it is structurally related, it is not a hygroscopic compound.

The structural similarity of sulfamic and sulfuric acids is indicated by the formulas showing their functional groups: $H_2N\text{-}SO_2\text{-}OH$ and $HO\text{-}SO_2\text{-}OH$, respectively. Perhaps a more appropriate formula for sulfamic acid in the crystalline state is that of the bipolar ion, $^{+}H_3N\text{-}SO_2\text{-}O^{-}$. Undoubtedly, the stability of this bipolar ion relative to that of the uncharged molecule accounts for the fact that sulfamic acid normally occurs as a solid, whereas sulfuric acid occurs as a liquid.

Sulfamic acid is readily soluble in water, dissolving to the extent of approximately 25 g in 100 g of water at 25°C. It behaves as a moderately strong electrolyte in water, thus conducting electricity readily in aqueous solutions. For the process of ionization in water, shown by Equation 5, the

$$H_2NSO_3H \rightarrow H_2NSO_3^{-} + H^{+} \qquad (5)$$

equilibrium constant at 25°C is 0.101. At a concentration of 0.1 M in water, sulfamic acid produces a pH of 1.25, only

slightly higher than the pH of 1.00 that is produced by sulfuric acid at the same concentration. Evidently, the bipolar ion mentioned above is far less important for sulfamic acid in solution than for the compound in the crystalline state.

Elevated Temperatures

At the elevated temperatures where sulfamic acid is used as a conditioning agent, the processes of melting, hydrolysis, and thermal decomposition may all be relevant to the mechanism of fly-ash conditioning. The importance of physical and chemical changes in the compound during the conditioning process has been stressed by various investigators. Lowe, for example, pointed out the original hypothesis that sulfamic acid serves as a source of sulfur trioxide through the reaction given previously in this report:[18]

$$H_2NSO_3H \rightarrow NH_3 + SO_3 \qquad (1)$$

Representatives of Apollo Chemical Corporation stress the importance of injecting their formulation of sulfamic acid at high temperatures to achieve volatilization, although they do not describe the nature of the volatilization process.[20,23]

The normal melting point of sulfamic acid is 205°C. Up to this temperature, dry sulfamic acid appears to be stable.[31] At elevated temperatures in the presence of water, however, the compound may undergo hydrolysis, yielding ammonium bisulfate as the product:

$$H_2NSO_3H + H_2O \rightarrow NH_4HSO_4 \qquad (6)$$

It is known that this process is accelerated as the temperature of sulfamic acid in aqueous solutions is increased.[29] It is possible that this process may also occur between dry sulfamic acid and water vapor at temperatures between the boiling point of water and the melting point of sulfamic acid (that is, between 100 and 205°C).

Various investigators have studied the thermal decomposition of sulfamic acid to fragments such as ammonia and sulfur trioxide. Halstead[31] performed one of the most comprehensive studies. This study was carried out with the purpose of explaining how sulfamic acid acts as a conditioning agent for fly ash. Halstead reported that heating sulfamic acid in a stream of dry nitrogen causes little volatilization below the melting point or above the melting point up to a temperature

of 323°C but then produces considerable volatilization between 323 and 467°C. The observed yield of sulfur trioxide is only about 0.2 mole per mole of sulfamic acid, rather than 1.0 mole as shown by Equation 1. The remaining sulfur in the starting material, about 0.8 mole, is released as sulfur dioxide as a result of an internal oxidation-reduction process in the residue that releases elemental nitrogen (N_2) along with the sulfur dioxide.

For a constant decomposition temperature of 397°C, Halstead concluded that molten sulfamic acid volatilizes through a series of decomposition reactions. The information given by Halstead is expressed by the reaction sequence given on the following page, which is based on one mole of molten sulfamic acid as the starting material. The first reaction (Equation 7) is the conversion of the melt to a molten mixture of two new compounds: a cyclic sulfur-nitrogen compound and ammonium bisulfate. The next reaction (Equation 8) evolves gaseous sulfur trioxide and again alters the composition of the melt, producing ammonium pyrosulfate and different sulfur-nitrogen compounds. Subsequently, a further reaction (Equation 9) evolves gaseous nitrogen, water, and sulfur dioxide and once more alters the composition of the melt. Finally, the residual melt remains constant in composition but evolves gaseous ammonia, nitrogen dioxide, water, and sulfur dioxide (Equation 10). When volatilization is complete, the net reaction is shown by the sum of Equations 7 through 10:

$$NH_2SO_3H(l) \rightarrow 0.167\ SO_3(g) + 0.833\ SO_2(g) \quad (11)$$
$$+ 0.500\ H_2O(g) + 0.083\ N_2(g) + 0.667\ NH_3(g) + 0.167\ NO_2(g)$$

Halstead did not report any information about the rates of the several reactions given above. However, rate data were obtained in the laboratory of American Electric Power Service Corporation for the volatilization of sulfamic acid in the commercial form used at the Cabin Creek Station. A sample of this material was held for 1 hr at various temperatures and the cumulative losses in weight were determined, with the results shown in Table 7.

The above information bearing on the stoichiometry and the rate of decomposition of sulfamic acid may or may not be applicable to the decomposition of this compound when it is dispersed as a powder in hot flue gas. First, with regard to stoichiometry, the presence of significant concentrations of water vapor and oxygen in flue gas may suppress the formation of ammonium pyrosultate (the anhydride of ammonium bisulfate, as shown in Equation 8), and the reduction of the sulfur

$$1.000\ NH_2SO_3H(l)$$

$$\downarrow$$

$$\{0.083\ (NHSO_2)_6 + 0.500\ NH_4HSO_4\}(l) \qquad (7)$$

$$\downarrow$$

$$0.167\ SO_3(g) + \{0.167\ NH_4HSO_4 + 0.0167\ (NH_4)_2S_2O_7 + 0.083\ (NH_2)_2SO_2 + 0.083\ NH_2(SO_2NH)_2SO_2NH_2\}(l) \qquad (8)$$

$$\downarrow$$

$$\{0.083\ N_2 + 0.167\ H_2O + 0.250\ SO_2\}(g) + \{0.167\ (NH_4)_2SO_4 + 0.167\ NH_4HSO_4 + 0.083\ NH_2(SO_2NH)_2SO_2NH_2\}(l) \qquad (9)$$

$$\downarrow$$

$$\{0.667\ NH_3 + 0.167\ NO_2 + 0.333\ H_2O + 0.583\ SO_2\}(g) \qquad (10)$$

REACTION SEQUENCE FOR THE DECOMPOSITION OF SULFAMIC ACID ABOVE ITS MELTING POINT[31]

Table 7. RESULTS OF A VOLATILIZATION STUDY OF A COMMERCIAL FORM OF SULFAMIC ACID

Temperature, °C	Cumulative weight loss, %
100	0
200	0
400	6
500	10
600	10(+)
700	11
900	30

trioxide constituent of sulfamic acid to sulfur dioxide, as shown in Equations 9 and 10. Second, with regard to rate, the dispersion of a fine powder might lead to much more rapid decomposition than that indicated by the above loss-in-weight data, which presumably were obtained with bulk powder resting in some type of vessel in a laboratory furnace.

CONDITIONING MECHANISMS

It must be assumed that in the pilot-plant and full-scale investigations of sulfamic acid described earlier in this paper the lowering of the electrical resistivity of the fly ash was one probable mechanism of conditioning. It is also necessary, however, to consider a space-charge effect and an increase in the cohesiveness of the ash as alternative mechanisms, as observed with ammonia conditioning.[13]

Lowering of the Electrical Resistivity of Fly Ash

The laboratory experiments of Dalmon and Tidy[15] included measurements of the resistivity of fly ash, which indicated that the resistivity was lowered by sulfamic acid conditioning. On the other hand, the full-scale precipitator studies in this country did not, unfortunately, include any measurements of resistivity. These studies did, however, yield data on fly-ash composition and precipitator electrical parameters that suggest conditioning by a lowering of resistivity. A question of both practical and theoretical interest is what chemical substances could have been responsible for this effect at the widely varying temperatures at which the sulfamic acid was injected and the treated fly ash was collected.

Successful results have been reported with sulfamic acid injected as an aqueous spray at temperatures of 165, 400, and 500°C. Successful trials of sulfamic acid have also been reported with the injection of the powdered solid at temperatures ranging from about 400 to 625°C. In view of the fact that the stability of sulfamic acid changes markedly through the range of temperatures that have been used for injection, different chemical substances undoubtedly participate in the conditioning of fly ash as the injection temperature is altered.

Low-Temperature Injection—

The lowest injection temperature that has been cited in this report, 165°C, is below the melting point of sulfamic acid and also below the range of temperatures that is required for molecular fragmentation of the compound. At this temperature, therefore, injection of an aqueous solution of sulfamic acid may leave a residue of small particles of the sulfamic acid to be coprecipitated with the fly ash after the liquid water of the solution has evaporated. Alternatively, during the process of injection, the sulfamic acid may undergo hydrolysis to ammonium bisulfate as illustrated in Equation 6.

The coprecipitation of discrete particles of sulfamic acid and fly ash conceivably could have lowered the effective resistivity of the ash. The basis for this statement is Dalmon and Tidy's finding that the coprecipitation of discrete particles of fly ash and another conditioning agent, sodium chloride, lowered the resistivity of the ash. Their publication includes the reproduction of a photomicrograph showing a large particle of fly ash partially coated with crystals of sodium chloride, all smaller than 1 μm in size.[15]

The formation of ammonium bisulfate and the coprecipitation of this compound with fly ash would undoubtedly have been a more effective process for lowering the resistivity than the coprecipitation of the original sulfamic acid. Above 144°C, ammonium bisulfate is a liquid that can spread over the surfaces of individual fly-ash particles, producing a continuous film of a conductive compound rather than a discontinuous coating of discrete crystals. (Different melting temperatures of the bisulfate have been reported by various investigators; here, the value cited is that reported by Kelley et al.,[32] which appears to be the most reliable.)

The low-temperature conditioning of fly ash with sulfamic acid through the action of liquid ammonium bisulfate has been postulated as an explanation for the effectiveness of sulfamic acid in the work of Dalmon and Tidy.[33] A critical aspect of the circumstances under which sulfamic acid was

employed by Dalmon and Tidy was the temperature of the precipitator, 145°C—just above the reported melting point of ammonium bisulfate.

High-Temperature Injection—

All of the injection temperatures for sulfamic acid above 165°C were above the melting point of the compound and high enough to decompose the compound through the sequence of reactions shown on page 26. Injection of sulfamic acid as a powdered solid undoubtedly was followed to some degree by this sequence of reactions. Injection of the conditioning agent in an aqueous solution, on the other hand, conceivably could have produced ammonium bisulfate by hydrolysis (Equation 6) as the water evaporated from the solution droplets.

The formation of some gaseous sulfur trioxide but, more importantly, the formation of a relatively large quantity of ammonium bisulfate at high temperatures (Equations 7 and 8) has been proposed as an explanation of sulfamic-acid conditioning with high-temperature injection.[33] Thus, the formation of ammonium bisulfate has been proposed as the key to the conditioning process at high temperatures as well as low temperatures of injection.

A matter of some concern that is related to the above conclusions is Dalmon and Tidy's failure to find ammonium and bisulfate ions on their conditioned fly ash in the 1:1 molar ratio that occurs in ammonium bisulfate.[15] As previously pointed out in this report, Dalmon and Tidy suggested that most of the ammonium ion was lost as ammonia gas as a result of the reaction between the surface film of ammonium bisulfate and basic constituents of the fly ash. Perhaps ammonium ion remained in the outermost layer of the deposit, which was not in physical contact with the basic constituents of the ash.

Conditioning through the Space-Charge Mechanism

It seems likely that conditioning by sulfamic acid through the space-charge mechanism will occur only if two temperature conditions are satisfied: (1) the compound is injected at a temperature that is high enough to cause molecular fragmentation to ammonia and sulfur trioxide as gaseous products and (2) the decomposition products subsequently reach a considerably lower temperature that permits the products to recombine in the presence of water vapor as fine particles of ammonium sulfate or ammonium bisulfate. If the injection temperature is low, molecular fragmentation will not occur, and only large particles with a low concentration by number will be introduced. On the other hand, if the temperature of the flue gas is not lowered sufficiently as the gas stream

approaches the precipitator, recombination of the molecular fragments will not be thermodynamically possible. The kinetic studies of Halstead[31] indicate that the injection temperature would probably have to be above 300°C. The thermodynamic data of Kelley et al.[32] indicate that the precipitator temperature would have to be as low as 195°C if ammonia and sulfur trioxide at concentrations of the order of 10 ppm are to react and produce ammonium sulfate or the temperature would have to be even lower, 173°C, if they are to produce ammonium bisulfate as an alternative product.

Both temperature conditions were satisfied in most of the investigations of sulfamic acid described in this report. The most outstanding exception occurred in the pilot-plant work of Dalmon and Tidy with the lower of two injection temperatures, 165°C.[15] Unfortunately, the available data do not provide any basis for determining whether the space-charge effect was a significant conditioning mechanism. However, the problem of air preheater plugging that was encountered by Buell[25] is comparable to the problem encountered in some studies of ammonia conditioning when the site of ammonia injection was upstream from the air preheater.[10,11] The similarity of these problems with the two conditioning agents suggests a possible similarity of conditioning mechanisms.

Conditioning through the Mechanism of Increasing the Cohesiveness of Fly Ash

Ammonium bisulfate, one of the decomposition products of sulfamic acid, may act as a conditioning agent by increasing the cohesiveness of fly ash,[34] particularly at precipitator temperature above 144°C where the compound exists as a liquid. The importance of this process, however, cannot be assessed because of the lack of pertinent data.

SECTION VIII

FUNDAMENTAL PROPERTIES AND CONDITIONING MECHANISMS OF AMMONIUM SULFATE AND AMMONIUM BISULFATE

PHYSICAL AND CHEMICAL PROPERTIES

The content of this section of the report parallels the content of the preceding section dealing with sulfamic acid. It consists of, first, a discussion of the properties of ammonium sulfate and ammonium bisulfate (particularly those related to fly-ash conditioning) and, second, a discussion of the mechanisms of conditioning by the two ammonium salts.

Ambient Temperatures[35,36]

At ambient temperatures, ammonium sulfate and ammonium bisulfate exhibit some of the same properties as sulfamic acid. Both compounds occur as white crystalline solids, and they are readily soluble in water, where they are strongly ionized and readily capable of conducting electricity.

In an aqueous solution, ammonium sulfate behaves as a weak acid as the result of the ionization of the ammonium ion:

$$NH_4^+ \dashrightarrow NH_3 + H^+ \qquad (12)$$

When dissolved in water, ammonium bisulfate is a significantly stronger acid than ammonium sulfate because of the ionization of the bisulfate ion:

$$HSO_4^- \dashrightarrow H^+ + SO_4^{-2} \qquad (13)$$

Approximate pH values of 0.1 M solutions of ammonium sulfate and ammonium bisulfate are 5.5 and 1.6, respectively.

Elevated Temperatures

Melting Points—

At elevated temperatures, ammonium sulfate melts without decomposition only in a closed system, and its melting point is reportedly to be around 510°C.[35] The compound decomposes

prior to melting in an open system, producing ammonia and ammonium bisulfate.[35] Ammonium bisulfate, on the other hand, melts without significant decomposition at a temperature of about 144°C.[32]

Equilibrium between Ammonium Sulfate and Ammonium Bisulfate—

The decomposition of ammonium sulfate to ammonia and ammonium bisulfate was shown earlier by Equation 4. The reaction is shown below with the physical states of the reactant and the products indicated (s = solid, l = liquid, and g = gas):

$$(NH_4)_2SO_4(s) \longrightarrow NH_3(g) + NH_4HSO_4(s,l) \qquad (4)$$

The dual notation for the physical states of ammonium bisulfate signifies that this reaction product is a solid below its melting point and a liquid above this temperature.

Kelley et al. have published thermodynamic data for the reaction shown by Equation 4;[32] their information on the equilbrium constants can be approximated as follows:

- Below the melting point of NH_4HSO_4, 144°C

$$\log K_4 = -5,659/T + 5.630$$

- Above the melting point of NH_4HSO_4

$$\log K_4 = -6,519/T + 7.693$$

Use of these equations yields the values in Table 8 for the partial pressure of ammonia in equilibrium with the two pure ammonium salts at selected temperatures ranging from 120 to 500°C.

Kijoura and Urano[37] and Rozenknop and Sedov[38] have published data from recent determinations of the partial pressure of ammonia in equilibrium with the two salts above the melting point of the bisulfate. The partial-pressure data from both of these sources are substantially higher than the data in Table 8 for the upper range of temperature. A possible explanation for the discrepancies is that neither of the later investigations actually yielded results to be compared with the predictions based on the paper of Kelley et al., which deals with a hypothetical system in which pure solid ammonium

Table 8. EQUILIBRIUM PARTIAL PRESSURES OF AMMONIA IN EQUILIBRIUM WITH AMMONIUM SULFATE AND AMMONIUM BISULFATE AT VARIOUS TEMPERATURES

Temperature, °C	Pressure of NH_3, atm
120	1.70×10^{-9}
144	1.15×10^{-8}
175	1.39×10^{-7}
200	8.15×10^{-7}
225	4.01×10^{-6}
300	2.07×10^{-4}
400	1.02×10^{-2}
500	1.82×10^{-1}

sulfate and pure liquid ammonium bisulfate are both present (that is, with a thermodynamic activity of unity for both). The mixtures used in the later investigations probably were a mixture of pure solid sulfate and a binary melt of the two salts in which the activity of the bisulfate was less than unity.

Equilibria between the Salts and Molecular Fragments—

Theoretically, it is possible for ammonium sulfate and ammonium bisulfate to decompose to the molecular fragments: ammonia, water, and sulfur trioxide. The formation of these constituent compounds from the salts has been shown previously by Equations 2 and 3, which are repeated below with the physical states of the reactants and the products indicated:

$$(NH_4)_2SO_4(s) \rightarrow 2NH_3(g) + H_2O(g) + SO_3(g) \quad (2)$$

$$NH_4HSO_4(s,l) \rightarrow NH_3(g) + H_2O(g) + SO_3(g) \quad (3)$$

If the temperature of flue gas does not exceed 300°C, the presence of approximately 10%-by-volume of water vapor will convert sulfur trioxide to sulfuric acid by this reaction:[39]

$$H_2O(g) + SO_3(g) \rightarrow H_2SO_4(g) \quad (14)$$

Hence, at temperatures below 300°C in a flue-gas environment, it is appropriate to write Equations 15 and 16 (below) in place of Equations 2 and 3.

$$(NH_4)_2SO_4(s) \rightarrow 2NH_3(g) + H_2SO_4(g) \quad (15)$$

$$NH_4HSO_4(s,l) \rightarrow NH_3(g) + H_2SO_4(g) \quad (16)$$

In the temperature range from 300 to 400°C, reactions leading to the production of both sulfur trioxide and sulfuric acid must be taken into account. However, if the temperature of flue gas exceeds 400°C, the water vapor in the flue gas will not significantly react with sulfur trioxide to form sulfuric acid. Hence, above 400°C, Equations 2 and 3 are more appropriate than Equations 15 and 16.

The above discussion ignores the possibility of reactions in which ammonia reduces sulfuric acid or sulfur trioxide to sulfur dioxide with the concomitant formation of elemental nitrogen:

$$2NH_3(g) + 3H_2SO_4(g) \rightarrow N_2(g) + 6H_2O(g) + 3SO_2(g) \quad (17)$$

$$2NH_3(g) + 3SO_2(g) \rightarrow N_2(g) + 3H_2O(g) + 3SO_2(g) \quad (18)$$

Both of these reactions are favored by thermodynamic factors through a wide range of temperatures;[32] however, they appear to be inconsequential for kinetic reasons except perhaps in the upper part of the range of temperatures discussed in the preceding paragraph.

Approximate equations that can be used for calculating the equilibrium constants of the reactions shown in Equations 2, 3, 14, 15, and 16 are given in Table 9. These equations are based on data published by Kelley et al. for the decompositions of ammonium sulfate and ammonium bisulfate[32] and published in JANAF Tables for the reaction of sulfur trioxide with water to produce sulfuric acid.[39] The principal basis for uncertainty in the use of these equations is the fact that Kelley et al. found it necessary to use approximate values of the thermodynamic properties of ammonium bisulfate because of the absence of experimental data for this compound.

Table 9. EQUATIONS FOR THE EQUILIBRIUM CONSTANTS ASSOCIATED WITH THE DECOMPOSITION REACTIONS OF AMMONIUM SULFATE AND AMMONIUM BISULFATE[a]

Temp, ≤ 144°C (T ≤ 417°K)	Temp, ≥ 144°C (T ≥ 417°K)
$\log K_2 = -23{,}353/T + 31.530$	$\log K_2 = -23{,}353/T + 31.530$
$\log K_3 = -17{,}694/T + 25.900$	$\log K_3 = -16{,}834/T + 23.837$
$\log K_{14} = 5{,}368/T - 8.139$	$\log K_{14} = 5{,}368/T - 8.139$
$\log K_{15} = -17{,}985/T + 23.391$	$\log K_{15} = -17{,}985/T + 23.391$
$\log K_{16} = -12{,}326/T + 17.761$	$\log K_{16} = -11{,}466/T + 15.698$

[a]These are only approximations because terms involving functions of temperature other than 1/T have been ignored.

The equations in Table 9 have been used to calculate the partial pressures of ammonia and sulfuric acid that would theoretically be produced by the decomposition of ammonium sulfate or ammonium bisulfate in a hypothetical flue-gas environment containing neither of these gaseous products prior to the introduction of the ammonium salt. (The flue-gas environment is described as hypothetical for, in actuality, it would contain a finite background concentration of sulfuric acid as a result of the partial combustion of sulfur in the coal to this compound.) The calculations were made with the assumption that at least a trace of excess ammonium salt would be present. The results of the calculations, covering the temperature range from 120 to 300°C, are given in Table 10.

Table 10. EQUILIBRIUM PARTIAL PRESSURES OF AMMONIA AND SULFURIC ACID IN EQUILIBRIUM WITH AMMONIUM SALTS AT VARIOUS TEMPERATURES

Temp, °C	$(NH_4)_2SO_4$		NH_4HSO_4
	$[NH_3]$, atm	$[H_2SO_4]$, atm	$[NH_3] = [H_2SO_4]$, atm
120	4.40×10^{-8}	2.20×10^{-8}	1.58×10^{-7}
144	3.32×10^{-7}	1.66×10^{-7}	1.26×10^{-6}
175	3.28×10^{-6}	1.64×10^{-6}	1.27×10^{-5}
200	1.67×10^{-5}	8.36×10^{-6}	5.33×10^{-5}
225	7.22×10^{-5}	3.61×10^{-5}	2.17×10^{-4}
300	2.72×10^{-3}	1.36×10^{-3}	6.98×10^{-4}

Mechanisms of Decomposition of the Salts as Observed Experimentally—

The thermal decompositions of ammonium sulfate and ammonium bisulfate have been studied by a number of investigators. However, the results of two investigations by Kiyoura and Urano[37] and by Halstead[40] appear to be most appropriate for discussion in this report.

Kiyoura and Urano determined differential thermal analysis (DTA) and thermogravimetric analysis (TGA) curves as ammonium sulfate or ammonium bisulfate was heated in a stream of air, sometimes with ammonia or water vapor added. They concluded that the first step in the decomposition was the release of ammonia gas and the formation of the compound triammonium hydrogen sulfate as a solid residue, which is stoichiometrically equivalent to the double salt of ammonium sulfate and ammonium bisulfate:

$$2(NH_4)_2SO_4(s) \rightarrow (NH_4)_3H(SO_4)_2(s) + NH_3(g) \qquad (19)$$

This reaction was said to be predominant below 170°C. The reaction usually given for the deammoniation of ammonium sulfate (previously shown by Equation 4), however, was said to be predominant above 170°C:

$$(NH_4)_2SO_4(s) \rightarrow NH_4HSO_4(l) + NH_3(g) \qquad (4)$$

Kiyoura and Urano found that liquid ammonium bisulfate released water vapor and produced ammonium pyrosulfate solid as the main reaction during heating at temperatures above 170°C:

$$2NH_4HSO_4(l) \rightarrow (NH_4)_2S_2O_7(s) + H_2O(g) \qquad (20)$$

They also reported the formation of small amounts of sulfamic acid in the solid residue and the formation of unspecified amounts of ammonia, sulfur trioxide, sulfur dioxide, sulfuric acid, hydrogen, and nitrogen in the gas phase.

Each of the reactions written above (shown by Equations 4, 19, and 20) was found to be reversible. That is, the addition of ammonia to the airstream passing over ammonium sulfate suppressed the deammoniation of this compound and the addition of water vapor suppressed the dehydration of ammonium bisulfate.

Each of the ammonium salts was heated at the rate of 4.0°C/min or sometimes at a slower rate. All of the TGA curves show that loss of weight by volatilization occurred slowly, regardless of the rate of heating. In air containing no added ammonia or water vapor, the heating rate of 4.0°C/min produced the losses in weight listed in Table 11 as the temperature reached values ranging from 200 to 400°C. In air containing one of the reaction products as an initial component, lower losses of weight were observed as the specified temperatures were reached.

Table 11. WEIGHT LOSSES BY VOLATILIZATION OF AMMONIUM SULFATE OR AMMONIUM BISULFATE AT A HEATING RATE OF 4.0°C/MIN

Compound	Temperature, °C	Cumulative weight loss, %
$(NH_4)_2SO_4$	200	1
	250	2
	300	15
	350	100
NH_4HSO_4	200	1
	250	3
	300	8
	350	25
	400	100

Halstead's experiments with ammonium sulfate in argon at a constant temperature of 400°C also showed the deammoniation of this compound (Equation 4) and the dehydration of the residue (Equation 20). These experiments also permitted a description of the reaction ultimately leading to complete volatilization of the residue from the reaction shown by Equation 20. Halstead concluded the overall reaction at 400°C could be expressed as follows:

$$3(NH_4)_2SO_4(s) \rightarrow 4NH_3(g) + 3SO_2(g) + 6H_2O(g) + N_2(g) \quad (21)$$

It is to be noted that no sulfur trioxide or sulfuric acid is shown as a reaction product.

There are apparent discrepancies between the above experimental findings and the previously discussed predictions from thermodynamic equations. At the present, it is not certain

how these discrepancies can be resolved, partly because the experimental conditions were substantially different from those prevailing in a flue-gas environment for which the thermodynamic predictions were made.

CONDITIONING MECHANISMS

Section VI of this report cited several instances where ammonium sulfate and ammonium bisulfate improved the collectibility of fly ash with high electrical resistivities. It also cited two instances where the ammonium salts improved the collectibility of fly ash with low to moderate resistivities. Thus, different mechanisms of conditioning were clearly in operation. Undoubtedly, lowering the resistivity was the primary mechanism of conditioning the high-resistivity ash. Tentatively, a space-charge effect and an alteration of the cohesiveness of fly ash are assumed to be important mechanisms with low- to moderate-resistivity ash.

Lowering the Electrical Resistivity of Fly Ash

The aspect of this conditioning mechanism that is of primary interest is the identification of the chemical substances that lower the resistivity of fly ash when ammonium sulfate or ammonium bisulfate is used as a flue-gas additive. The identification of the active substances is a matter of importance as in the instance of sulfamic-acid conditioning because of the wide range of injection temperatures that have been used for the two ammonium salts. As stated in Section VI, gas streams containing high-resistivity ash have been treated with the ammonium salts at temperatures ranging from 130 to 400°C.

Low-Temperature Injection—

Ammonium sulfate and ammonium bisulfate have been injected into the flue gas entering two pilot-plant precipitators and two full-scale precipitators in the form of aqueous solutions at comparatively low temperatures—a minimum of 130°C and a maximum of 165°C. Reference is made to the data given previously in Tables 8, 10, and 11 showing theoretical equilibrium partial pressures and rates of formation of the decomposition products of the ammonium salts (ammonia and sulfuric acid in the gaseous state). The data in these tables leave little reason to postulate that appreciable decomposition of either ammonium salt occurred at injection temperatures in the range of concern, 130 to 165°C. It seems probable, therefore, that each flue-gas additive was coprecipitated with the fly ash. It is possible, of course, that some chemical process

occurred within the coprecipitate such as the release of ammonia as a result of the action of basic constituents of the ash, as described by Dalmon and Tidy.[15]

A coprecipitate of ammonium sulfate and fly ash can be visualized as an intimate mixture of discrete particles of each substance (comparable to the coprecipitate of sodium chloride and fly ash discussed in Section VII). It is somewhat surprising that such a mixture could have the same resistivity as fly ash conditioned with sulfur trioxide, where the surface of the ash should be much more uniformly coated with the conditioning agent. Yet, according to Dalmon and Tidy, ash conditioned with the two agents has the same resistivity if the ratio of moles of conditioning agent to the weight of ash is the same.[15]

A mixture of ammonium bisulfate and fly ash precipitated at a temperature above the melting point of the bisulfate might easily consist of ash particles uniformly coated with the conditioning agent. It is a matter of record that in the only instances where the bisulfate was used as a flue-gas additive in the low-temperature range the injection temperature and the precipitator temperature were still above the melting point of the bisulfate.[15,19]

High-Temperature Injection—

The highest injection temperatures cited in Section VII were 300 and 400°C for ammonium sulfate and 400°C for ammonium bisulfate. Reference to Tables 10 and 11 will show that complete decomposition of both compounds was thermodynamically feasible at injected concentrations of the order of 20 ppm by volume and that rapid attainment of equilibrium was also possible. The primary question about the mechanism of conditioning is what phenomena subsequently occurred as the flue gas was cooled before entering the precipitator.

One possibility is that the decomposition products recombined through reversal of the high-temperature reactions, yielding a fume of ammonium sulfate or ammonium bisulfate. Electrical charging of the fume in the precipitator could have enhanced the space-charge component of the electric field and thus produced an undesirable increase in the rate of sparking if no change occurred in the high-resistivity fly ash.

Another phenomenon seems more probable in view of the fact that improvements in precipitator efficiency were achieved. That is, a sufficient quantity of the sulfuric acid vapor produced at the injection temperature was collected by the fly ash and thus lowered the resistivity.

Other Mechanisms of Conditioning

Other mechanisms of conditioning by ammonium sulfate and ammonium bisulfate probably included, on occasion, a space-charge effect and an alteration of the cohesiveness of fly ash. These mechanisms have already been discussed in connection with conditioning by sulfamic acid (Section VII), and only a few of the previous comments need be stressed in regard to the ammonium salts. First, as suggested on the previous page, the space-charge effect was of likely importance only with high-temperature injection (capable of fragmenting the salts to their gaseous constituents) and with relatively low-temperature precipitation (capable of allowing the gases to be present after recombination as particulates at high concentrations on a number basis). Second, the effect on cohesiveness was of most likely importance with low- or moderate-resistivity ash, for which reentrainment was not restrained sufficiently by electric force.

SECTION IX

ECONOMIC ASPECTS OF SULFAMIC ACID, AMMONIUM SULFATE, AND AMMONIUM BISULFATE AS CONDITIONING AGENTS

Dalmon and Tidy made a comparison of the relative costs of sulfur trioxide, sulfuric acid, sulfamic acid, ammonium sulfate, and ammonium bisulfate as conditioning agents.[15] Their first basis of comparison was the purchase price per mole of sulfur trioxide theoretically available from one mole of each compound. Their second basis of comparison took into account the efficiency of pickup of each agent by fly ash as observed experimentally. The results of the comparisons are given in Table 12. The relative costs given in this table indicate that sulfamic acid and ammonium bisulfate have a decidedly adverse competitive position resulting from both purchase price and effectiveness.

Table 12. RELATIVE COSTS OF SULFUR TRIOXIDE, SULFAMIC ACID, AND RELATED CONDITIONING AGENTS[15]

Conditioning agent	Cost per mole purchased	Cost for effective use
Sulfur trioxide	1.0	1.0
Sulfuric acid	0.6	1.1
Sulfamic acid	5.7	11.4
Ammonium sulfate	1.1	2.4
Ammonium bisulfate	5.5	11.1

Capital and operating costs were not taken into account in the above comparisons. Dalmon and Tidy pointed out that these items of cost would be much lower for any of the alternatives to sulfur trioxide that can be injected as sprays of dilute aqueous solutions or as powdered solids. Even so, these investigators regarded the direct costs of sulfamic acid and ammonium bisulfate as too great to be offset by lower capital costs; thus, they concluded that only sulfuric acid and ammonium sulfate would be competitive with sulfur trioxide.

The current relative prices in the United States of all of the conditioning agents except ammonium bisulfate appear to be about the same as those cited by Dalmon and Tidy.[41,42] No price information for ammonium bisulfate as a chemical commodity appears to be available currently; indeed, the availability of this compound is questionable, for no supplier of the compound is cited in several current chemical purchasing guides.[43-45]

Despite the unfavorable cost of sulfamic acid, the Apollo Chemical Corporation apparently is having significant success in marketing blends of this conditioning agent with other compounds. For comparable rates of injection on a molar basis, the relative costs of Apollo's dry chemical and sulfur trioxide in a 200-MW power station have been estimated by the supplier[23] as shown in Table 13. The figures in this table indicate that the lower capital cost of injecting the Apollo agent offsets the higher cost of the agent and make the total annual cost of using this agent lower than that of using sulfur trioxide. These figures are based, however, on low injection rates producing additive concentrations in flue gas of only about 7.5 ppm by volume. It seems likely that if higher injection rates were needed the capital costs would increase less sharply than the additive costs and the injection of sulfur trioxide would become more economical.

Table 13. RELATIVE COSTS OF CONDITIONING BY SULFUR TRIOXIDE AND A COMMERCIAL FORM OF SULFAMIC ACID[23]

Source of cost	Cost per year[a]	
	Sulfamic acid	Sulfur trioxide
Capital	$ 4,000	$100,000
Conditioning agent	75,600	11,880
Maintenance	10,000	25,000
	$89,600	$136,880

[a]Power-plant size, 200 MW.

A representative of the utility industry[21] with experience in conditioning with both sulfur trioxide and sulfamic acid has challenged the validity of the comparison given in Table 13 on the basis of reagent costs. He has asserted that the assumed rate of addition of sulfamic acid is impractically low and that the assumed unit cost of sulfur trioxide is higher than the cost paid by his company. The point regarding the assumed rate of addition of sulfamic acid is essentially

the same as the point raised in the preceding paragraph; it implies that the indicated cost advantage of sulfamic acid vanishes if, for example, the rate of addition is necessarily twice the value assumed.

The figure given in Table 13 for the capital cost of conditioning with sulfur trioxide ($100,000) is about four times the capital cost estimated by Southern Research Institute ($24,500) for conditioning with 10 ppm of sulfur trioxide in a slightly larger plant (250 MW rather than 200 MW).[9] The estimate by the Institute was made in 1971, whereas that given in Table 13 was made in 1974. The effect of inflation over the 3-yr period would account for part of the difference in estimated capital costs. Still, the difference in estimates appears to be too large to be reconciled in terms of the effect of inflation. Unfortunately, the background data used in computing the figure in Table 13 are not available, and the difference between this figure and the earlier estimate cannot be satisfactorily explained.

No comparative cost data for conditioning with ammonium sulfate and sulfur trioxide appear to have been published. It seems likely, however, that ammonium sulfate would be an economical alternative to sulfur trioxide as a result of the lower capital cost of an injection system for the ammonium salt and the slight difference in costs of purchasing the salt and the sulfur trioxide.

SECTION X

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SECTION XI

APPENDIX. COMPOSITION OF A COMMERCIAL CONDITIONING AGENT BASED ON SULFAMIC ACID

Although representatives of Apollo Chemical Corporation acknowledge that their dry and liquid conditioning agents known as Coaltrol PPA-30 and Coaltrol LPA-40 contain sulfamic acid as a major constituent, they prefer to describe their agents as activated blends of chemical agents.[20] On one occasion, they described the additive used as a dry solid or in an aqueous solution as a blend of "amines and nitrogen-containing inorganic compounds combined with specific cations that are synergistic with the N-H cations." On the same occasion, they asserted that the additive is custom-blended for individual boilers and that variables determining the blend are the amounts of sulfur, sodium, and iron in the coal, the overall ratio of basic to acidic constituents in the coal, and the total ash content of the coal.[23]

Analyses of samples of Coaltrol PPA-30 have been made in the laboratories of the American Electric Power Service Corporation, the Buell Division of Envirotech Corporation, and Southern Research Institute. The results of these analyses are in essential agreement. They do not reflect any significant variation in the compositions of the samples analyzed, although the supplier of the agent asserts that the composition is changed to satisfy specific boiler requirements.

Analyses of samples of Coaltrol PPA-30 by the American Electric Power Service Corporation indicate that the agent consists of about 90%-by-weight sulfamic acid and 10%-by-weight manganous sulfate monohydrate ($MnSO_4 \cdot H_2O$).[21] These analyses consisted of determinations of a large number of elements, especially metals; a determination of the infrared spectrum; and a comparison of the physical properties of the agent with a blend of sulfamic acid and the hydrate of manganous sulfate.

Analysis in the Buell laboratory confirmed that sulfamic acid accounted for 90% of the conditioning agent.[25] The balance of the agent was reported as manganese dioxide (MnO_2). Although the presence of a compound of manganese seems likely, the presence of the dioxide would be inconsistent with the water-solubility of the agent.

Additional analyses at Southern Research Institute led to the following results: (1) the agent was found to be almost completely water-soluble in the weight ratio of 1 part of the solid to 10 parts of water (only about 0.8% of the solid failed to dissolve); (2) infrared and nuclear magnetic resonance spectra of the agent showed that sulfamic acid was the predominant component; (3) weight percentages of hydrogen and nitrogen were consistent with the occurrence of sulfamic acid as the primary component; and (4) titration of an aqueous solution with sodium hydroxide confirmed that sulfamic acid was the principal component (based on the calculated equivalent weight of the agent as an acid), but it also indicated that a relatively small amount of metal ion forming a reddish-brown precipitate in an acidic pH region (perhaps ferric or manganic ion) was also present.